Modelling Vapor-Liquid Equilibria of Binary Carbon Dioxide-Alkyl Carbonate Mixture Systems

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Abstract

This study is focused on modeling phase behavior of carbon dioxide(CO_2) + dimethyl carbonate system for the direct synthesis of DMC starting from CO_2. CO_2 + diethyl carbonate system was also represented to investigate the behavior of alkyl carbonate in the CO_2 media. The experimental data [17] were correlated by Peng-Robinson equation of state (PR EOS) using van der Waals one fluid mixing rule, PR EOS using Wong-Sandler mixing rule with NRTL and multi-fluid nonrandom lattice fluid (MF-NLF) model. The thermodynamic models represented the experimental data well.

Keywords : Vapor-liquid equilibrium; Carbon dioxide; Dimethyl carbonate; Diethyl carbonate; Equation of state

1. Introduction

Dimethyl carbonate (DMC) is a good nontoxic substitute for corrosive and toxic dimethyl sulfate, methyl halide and phosgene in methylation and carbonylation reactions, respectively [1-3]. As a non-aqueous electrolyte component, it is applied to the lithium rechargeable batteries [4]. It is used as an intermediate for preparing the carbamates, isocyanates and polycarbonates [3,4] and also used as a fuel additive [5] and solvents [3].

There have been five methods for synthesis of DMC. The first method is the phosgenation of methanol. This method was important to synthesize DMC until the 1980s, but this process was limited because toxic and corrosive chemicals, such as phosgene, hydrogen chloride, were used or generated. The second method is the oxy-carbonylation of methanol. This method was developed by EniChem and was based on the catalytic reaction of methanol with oxygen and carbon monoxide. The third method is the carbonylation of methyl nitrile developed by UBE. Carbon monoxide, oxygen and methanol as raw materials are used in this process. The forth method is the transesterification of ethylene carbonate with methanol [1-3]. The fifth method is the direct synthesis starting from carbon dioxide (CO_2). In the past decade, many research groups have made a study of the synthesis method [6-10]. We were also interested in this direct synthesis method, because of various advantages. Unlike other methods used or produced toxic or corrosive chemicals, this method is used CO_2 and methanol as raw materials and produced DMC and water. CO_2 is an environmentally benign and thermodynamically stable compound. Moreover, it is nontoxic, nonflammable and cheap, and its reactivity in the supercritical region is dramatically increased. Besides, separation from the reaction mixture is relatively easy.

Predicting phase behavior is important to design new processes and to find optimum operating conditions for the separation and reaction. Although experiment is an accurate method to study vapor-liquid equilibria, measurements of phase equilibiria require long time and money. The aim of this study is to propose the optimum thermodynamic model for CO_2 + DMC system for the direct synthesis of DMC from CO_2, and to investigate the phase behavior of alkyl carbonate in the CO_2 media. To research in this study, CO_2 + diethyl carbonate (DEC) system was also calculated.

2. Thermodynamic Models

Peng-Robinson equation of state (PR EOS) using van der Waals one fluid mixing rule [11], PR EOS using Wong-Sandler mixing rule [12] with NRTL [13] (PRWS-NRTL) and multi-fluid nonrandom lattice fluid (MF-NLF) model [14-16] are used to model the phase equilibria of CO_2 + alkyl carbonate systems.

2.1. Peng-Robinson equation of state

Peng-Robinson equation of state is as follows.

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

$$a(T) = \left(0.45724\frac{R^2T_c^2}{P_c}\right)\alpha(T) \tag{2}$$

$$b(T_c) = 0.07780\frac{RT_c}{P_c} \tag{3}$$

$$\alpha(T) = \left[1+\kappa\left(1-\sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{4}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

where Tc and Pc are the critical temperature and the critical pressure of the pure substance, respectively, and ω is the acentric factor. These parameters are listed in Table 1.

The van der Waals one fluid mixing rule used in this study is given by

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{6}$$

$$b_m = \sum_i x_i b_i \tag{7}$$

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{8}$$

where k_{ij} is the binary interaction parameter. It was used to regress the experimental vapor liquid equilibrium data. Subscript m denotes mixture. Additionally, Wong-Sandler mixing rule is represented as

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{CRT}} \tag{9}$$

$$a_m = b_m \left(\sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \right) \tag{10}$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}) \tag{11}$$

where $C = ln(\sqrt{2} - 1)/\sqrt{2}$ for the PR EOS. Because the excess Helmholtz free energy of mixing at infinite pressure is assumed equal to the excess Gibbs free energy (G^E) at low pressure, the G^E model is used in place of A_∞^E. We used NRTL model as an G^E model in this study.

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_i x_i \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} \tag{12}$$

$$G_{ij} = exp(-\alpha_{ij} \tau_{ij}) \qquad \alpha_{ij} = \alpha_{ji} \tag{13}$$

where τ_{ij} and τ_{ji} are the interaction parameters and α is the nonrandomness parameter.

2.2. MF-NLF

The general expression of the MF-NLF model can be written as

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2} ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - ln(1-\rho) + \frac{z}{2}\sum_{i=1}^{c}\theta_i\left(\frac{\tau_{0i}}{\sum_{k=0}^{c}\theta_k\tau_{ki}}-1\right)\right\} \quad (14)$$

where $q_M = \sum x_i q_i$, $r_M = \sum x_i r_i$, $r_i = V^* / V_H$, $\rho = \sum \rho_i$ and $\rho_i = N_i r_i / N_r = V^* / V$.

$$\varepsilon_{11} / k = E_a + E_b(T - T_0) + E_c\left(T\, ln\frac{T_0}{T} + T - T_0\right) \quad (15)$$

$$r_1 = R_a + R_b(T - T_0) + R_c\left(T\, ln\frac{T_0}{T} + T - T_0\right) \quad (16)$$

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}(1 - k_{12}) \quad (17)$$

where k_{12} is an binary interaction parameter.

3. **Results and discussion**

The experimental data of CO_2 + DMC system at 340.27, 330.30, 320.36 and 310.27K and CO_2 + DEC system at 340.29, 330.33 and 320.32K measured by Im et al. [17] were chosen for this study. The size parameters and the energy parameters of the DMC and DEC are obtained by using vapor pressure data and liquid density data, which were taken from the DIPPR database [20]. The size and energy parameters of CO_2 reported in [16] were used. These estimated values are listed in Table 2. The binary interaction parameter (k_{ij}) of each EOS and NRTL parameters (τ_{ij} and τ_{ji}) was estimated by regressing the experimental vapor liquid equilibrium data. The α_{ij} value of NRTL model was fixed as 0.3 for vapor-liquid equilibria. We used simplex algorithm to minimize the objective function (OF) which is as follows.

$$OF = \sum_{i}^{N}\left|\frac{P_{\exp} - P_{cal}}{P_{\exp}}\right| \quad (18)$$

where N is the number of experimental data points and $P_{\exp}$ and P_{cal} are the experimental and the calculated pressures, respectively. We optimized the adjustable parameters at each temperature of the VLE and at whole temperature ranges of the experimental data, respectively. The binary interaction parameters of each EOS and NRTL parameters for the CO_2 + alkyl carbonate systems are summarized in Table 2. The absolute average deviation of pressure (AADP) for the pressure is also given in Table 2. Figure 1. and 2. show experimental data and calculated results for CO_2 + DMC system and CO_2 + DEC system, respectively. The PRWS-NRTL model was obtained better agreement with the experimental VLE data than that of the PR EOS and the MF-NLF model. All equations correlate well with the data at low pressure, but the PR-EOS

and the MF-NLF model overestimate the pressure as approaching the critical region. This trend is extreme as increasing temperature. However, AADP of the MF-NLF model is about 2~3%, but on the other hand that of the PR-EOS is below 2%. Joung et al. [16] reported that the reason of that was due to mean-field approximation of the r-mer lattice statistical-mechanical theory. Therefore, it is limited in the critical region.

The binary interaction parameter (k_{ij}) of PR EOS is –0.0139 for CO_2 + DMC system and –0.0223 for CO_2 + DEC system. It seems that DEC is slightly more interactive with CO_2 than DMC.

4. Conclusion

Experimental VLE data reported by Im et al. were correlated by the PR EOS, the PRWS-NRTL model and the MF-NLF. Although PR EOS and MF-NLF model had some inaccuracies in the critical region, relatively good results are obtained. Among the thermodynamic models in this study, the PRWS-NRTL model provided the best fit with the experimental VLE data for CO_2 + alkyl carbonate systems.

List of symbols

a	equation of state energy parameter
b	equation of state excluded volume parameter
G	excess Gibbs energy
k	binary interaction coefficient
P	pressure
R	universal gas constant
T	temperature
T_R	reduced temperature (T/T_c)
x	mol fraction (liquid phase)
y	mol fraction vapor phase

Greek letters

α	NRTL model parameter
τ	NRTL model parameter
ω	acentric factor
ρ	total segment fraction

ε interaction energy for i-j segment contacts (J)

θ surface area fraction of component i

Superscripts

E excess property

Subscripts

cal calculated value

exp experimental value

i,j molecular species

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Table 1. Physical Properties

	CO_2	$C_3H_6O_3$	$C_5H_{10}O_3$
T_c / K	304.12[a]	557.0[a]	576.0[b]
P_c / bar	73.74[a]	48.0[a]	33.9[b]
ω	0.225[a]	0.336[a]	0.485[b]

[a] Reference 18. [b] Reference 19.

Table 2. Coefficients of molecular parameters for MF-NLF model

Chemicals	E_a	E_b	E_c	R_a	R_b	R_c
CO_2	85.91302	-0.10298	-0.36562	3.51652	0.00146	-0.00134
$C_3H_6O_3$	128.9852	-0.06266	-0.12880	7.77519	0.01460	-0.02049
$C_5H_{10}O_3$	117.1420	-0.04170	-0.15304	10.99237	0.00810	0.01776

Table 3. Optimized parameters

System	Model	T / K	k_{ij}	τ_{12}	τ_{21}	AAD
CO_2+DMC	P-R	310.27	-0.0135			0.98
		320.36	-0.0107			1.68
		330.30	-0.0150			2.26
		340.27	-0.0152			2.68
		overall	-0.0139			2.03
	PRWS-	310.27	0.3639	-0.5844	0.6343	0.35
	NRTL	320.36	0.3678	-0.5698	0.6669	0.42
		330.30	0.3622	-0.5632	0.6543	0.59
		340.27	0.3662	-0.5650	0.6671	1.03
		overall	0.3623	-0.5597	0.6590	0.78
	MF-NLF	310.27	-0.0158			2.13
		320.36	-0.0137			2.64
		330.30	-0.0159			2.90
		340.27	-0.0123			3.10
		overall	-0.0158			2.76
CO_2+DEC	P-R	320.32	-0.0223			1.83
		330.33	-0.0223			1.09
		340.29	-0.0216			1.11
		overall	-0.0223			1.34
	PRWS-	320.32	0.5008	-0.7838	0.8984	1.25
	NRTL	330.33	0.5045	-0.7981	0.8944	0.43
		340.29	0.5074	-0.8008	0.9017	0.56
		overall	0.5034	-0.7908	0.8994	0.83
	MF-NLF	320.32	0.0012			2.52
		330.33	0.0034			1.75
		340.29	0.0047			1.74
		overall	0.0014			2.16

$$AAD(\%) = (100 / N)\sum_{i}^{N} \left| P_{i(\exp)} - P_{i(cal)} \right| / P_{i(\exp)}$$

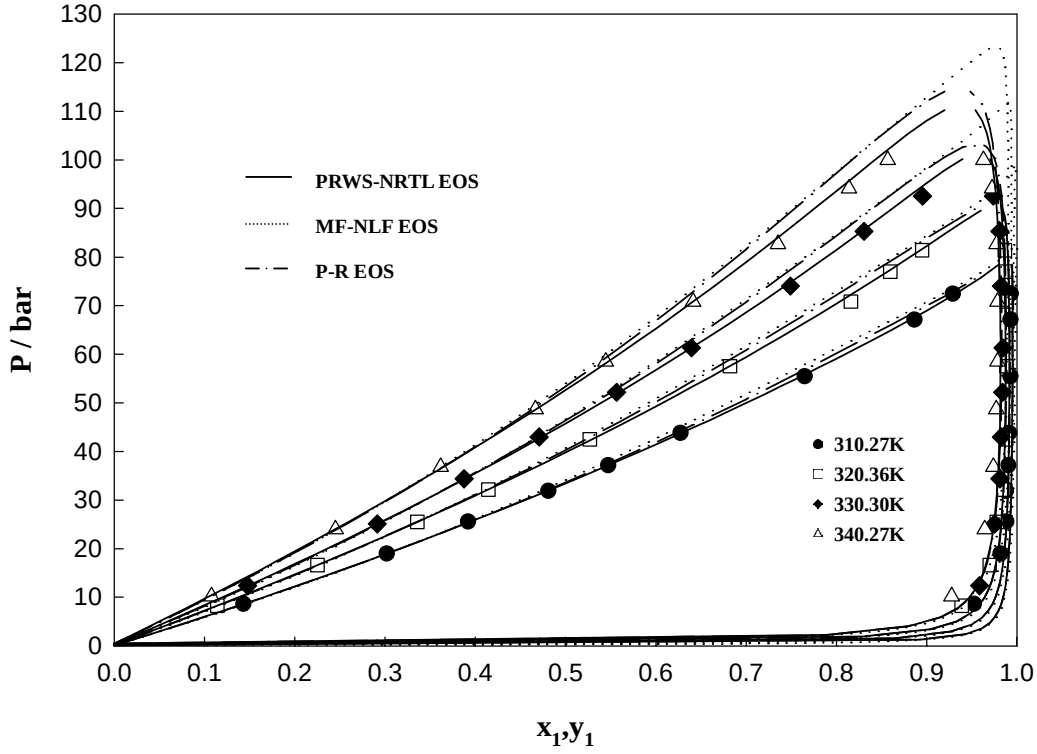

Fig. 1. Vapor-liquid equilibria of the CO_2 (1) + DMC (2) system

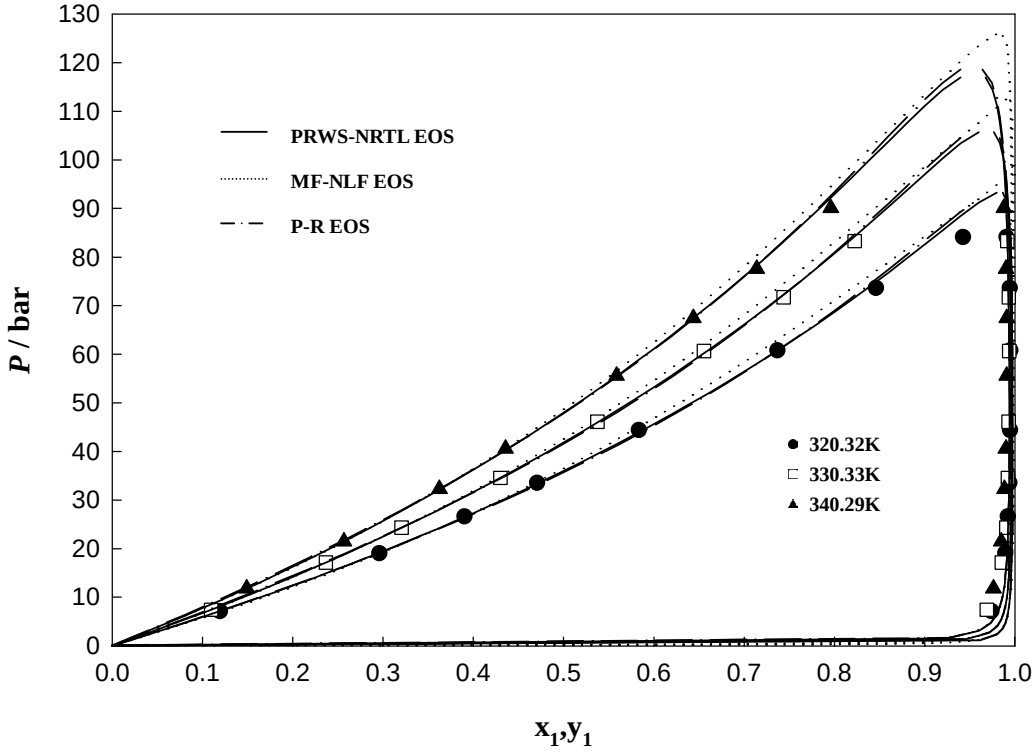

Fig. 2. Vapor-liquid equilibria of the CO_2 (1) + DEC (2) system